

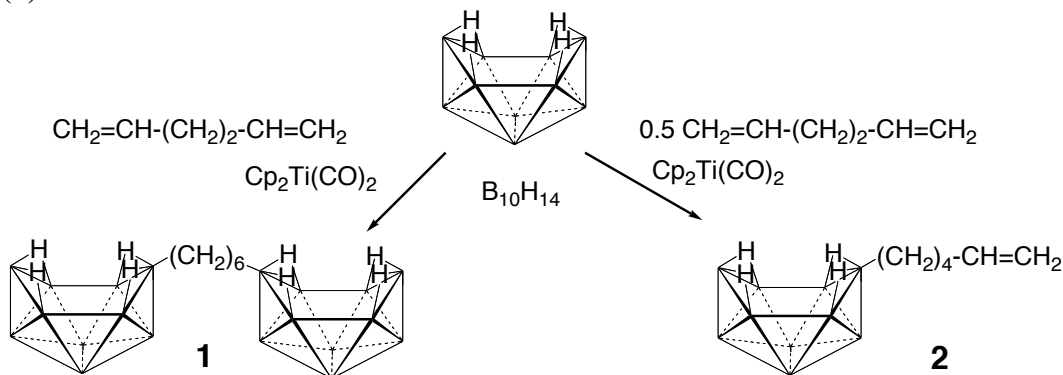
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13. ABSTRACT (Maximum 200 Words) The objective this AFOSR sponsored project was to design, synthesize and explore the materials applications of new, processable single-source chemical precursors to nonoxide ceramics that allow the formation of these technologically important materials in forms that have been unattainable with conventional methods. Research was focused on the development of new precursor routes to a number of ultra high temperature ceramics, including hafnium and zirconium -boride, -carbide and -nitride materials, and on the use of electrostatic spinning and diatom-templating methods, in conjunction with newly designed preceramic polymers, to achieve the formation of nano-structured ceramic materials.				
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CHEMICAL ROUTES TO CERAMICS WITH TUNABLE PROPERTIES AND STRUCTURES

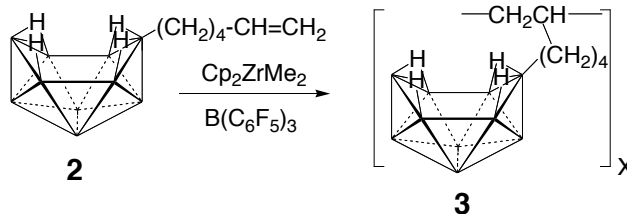
For the past three years, this research program was focused on the design, syntheses and applications of new processible chemical precursors to advanced ceramics, including boron carbide, silicon carbide and boron-carbide/silicon-carbide composites that would allow the formation of these technologically important materials in forms, including nanostructures, that were unattainable with conventional methods. Major achievements include: (1) the utilization of newly developed titanium-catalyzed decaborane olefin-hydroboration¹ and zirconium-catalyzed alkenylpolyborane polymerization² reactions to produce new highly-processible molecular and polymeric single-source precursors to boron carbide;^{3,4} (2) the development of more efficient “second-generation” precursors using ruthenium-catalyzed ring opening metathesis polymerizations (ROMP) of polyboranes substituted with cyclic olefins;^{4,5,6} (3) the design and synthesis of a new poly(borocarbosilane) polymer that has proven to be an excellent processible single-source precursor to dense silicon carbide ceramics;⁷ (4) a new precursor method of preparing two-phase toughened SiC/BN ceramic composite materials;^{8,9} and (5) the demonstration that many of the newly developed precursors can be used to form nanostructured materials, including nanofibers, nanocylinders and nanoporous ceramics.^{3,4,10,11,12} These accomplishments are discussed in more detail in the following sections.

Early Metal Catalyzed Hydroboration and Alkenylpolyborane Polymerization Reactions: New Routes to Molecular and Polymeric Boron Carbide Precursors

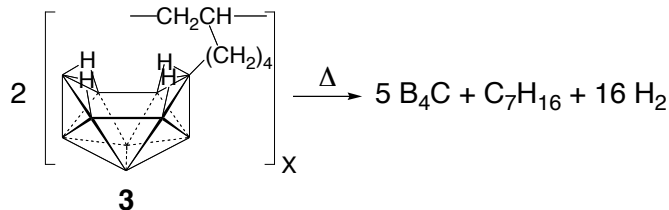
We reported¹ that the titanium catalyzed hydroboration reactions of decaborane with 1,5-hexadiene provide, depending upon the reaction stoichiometry, excellent yields (>88%) of either the linked-cage 6,6'-(CH₂)₆-(B₁₀H₁₃)₂ (**1**) or the hexenyl-substituted derivative 6-CH₂=CH(CH₂)₄-B₁₀H₁₃ (**2**).



We also demonstrated that 6-hexenyl-decaborane can be readily polymerized by the $(C_5H_5)_2ZrMe_2/B(C_6F_5)_3$ catalyst system to give excellent yields of a tractable polymer with molecular weights (determined by viscometry) of $M_n = 3950$ and $M_w = 5860$ ($M_w/M_n = 1.48$). The spectroscopic data support an inorganic/organic hybrid structure consisting of a polyolefin-backbone with pendant decaboranes.

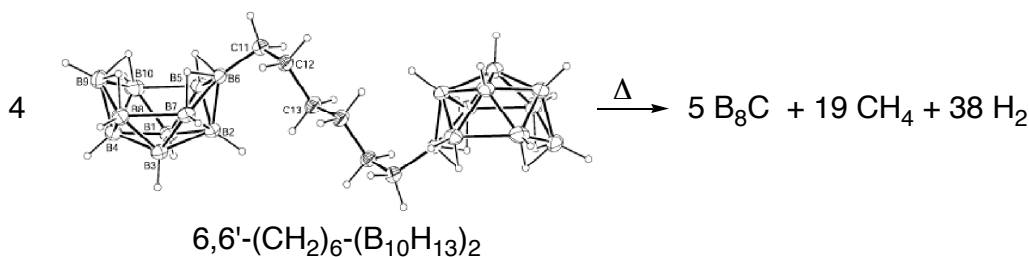


The poly(hexenyldecaborane) Tg's are in the 50-60°C range and polymer decomposition does not begin until ~225°C. Thus, these polymers are stable as melts.



The boron carbide ceramics obtained upon pyrolyses of the polymer to 1000°C are amorphous, but those heated at 1250°C exhibited the onset of boron carbide crystallization and their diffuse reflectance infrared spectra showed the characteristic boron carbide bands. Highly crystalline materials were obtained by heating at 1850°C. Elemental analyses of the ceramics confirm B₄C compositions. Boron carbide can have a range of compositions ranging from 8.8 to 20 atom% carbon and the ceramics derived from the poly(hexenyldecaborane) are thus on the “carbon-rich” side.

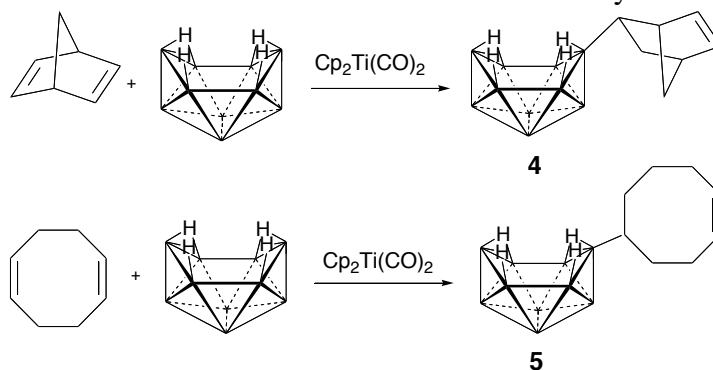
The compound 6,6'-(CH₂)₆-(B₁₀H₁₃)₂ **1** was also shown to be an excellent single-source molecular precursor to boron-rich boron carbide. Its ceramic-conversion reaction begins near 220°C and is essentially complete by 400°C. Samples of **1** heated at 1025°C again exhibited the characteristic boron carbide diffraction pattern and DRIFT spectra, but since the boron to carbon ratio (20:6) in 6,6'-(CH₂)₆-(B₁₀H₁₃)₂ is much higher than that in the poly(hexenyldecaborane) (10:6), “boron-rich” B_{7.7}C and B_{8.3}C boron carbide compositions were achieved.



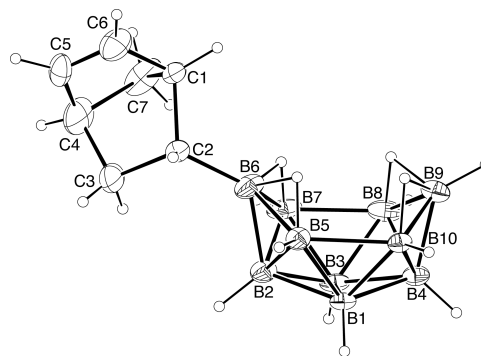
Because of its high-temperature stability, high hardness, high cross-section for neutron capture, and excellent high-temperature thermoelectric properties, boron carbide has numerous applications, including uses as an abrasive wear-resistant material, ceramic armor, a neutron moderator in nuclear reactors, and, potentially, for power generation in deep space flight applications.^{13,14} While boron carbide powders are easily made by the direct reaction of the elements at high temperatures, both poly(hexenyldecaborane) and **1** have proven to be important new chemical precursors for the production on boron carbide in processed forms including, as discussed more fully in a later section, nanostructured materials.

New Routes to Organodecaborane Polymers via Ruthenium-Catalyzed Ring Opening Metathesis Polymerization

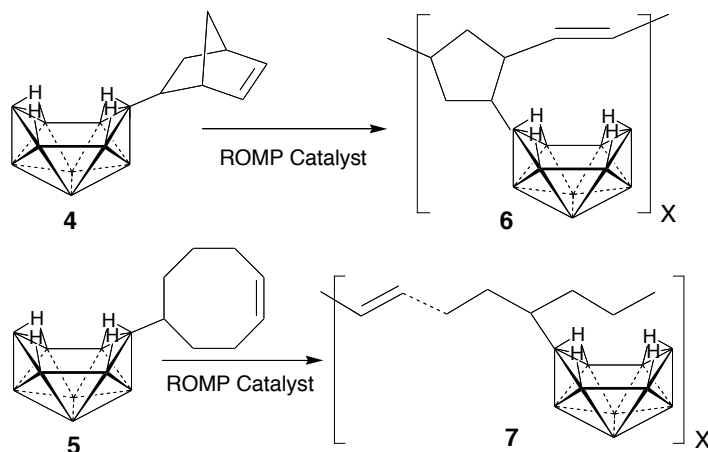
We demonstrated that ruthenium-catalyzed ring opening metathesis polymerization (ROMP) of organodecaboranes containing cyclic-olefin substituents provides a new efficient route to poly(organodecaborane) polymers which have much higher molecular weights than those previously attained.^{4,5,6} As shown in equations below, the high yield syntheses of the key decaboranyl-substituted norbornene and cyclooctene monomers were achieved by employing the titanium-catalyzed reaction of decaborane with norbornadiene and cyclooctadiene, respectively.



Typical conditions involved the reaction of a large excess of the olefin with decaborane in the presence of ~3 mol% catalyst at 90°C for 72 h. The products were easily isolated in pure form and excellent yields (**4**, 98% and **5**, 96%) from the metal catalyst by filtration through silica gel. As shown in the figure, a single crystal X-ray determination of **4** confirmed a 6-substituted norbornenyl-decaborane structure resulting from the titanium-catalyzed hydroboration of the norbornadiene C5-C6 double bond.



Because of their air stability and tolerance to various functional groups, “Grubbs-type” ROMP catalysts, $\text{Cl}_2\text{Ru}(=\text{CHPh})(\text{PCy}_3)_2$, **I** or H_2IMes (**II**) appeared to be ideal candidates for the syntheses of polyborane polymers.¹⁵

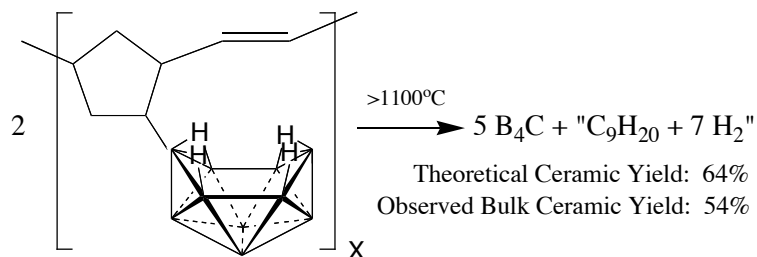


Both the **I** and **II** catalysts polymerized **4** and **5** efficiently, giving ~90% conversions in the 1 h reaction time. As shown in the Table below for the polymerization of **4**, molecular weight studies by size exclusion chromatography employing both multi-angle light scattering and DRI detectors showed that molecular weights with M_n in excess of 30 KDa can be readily obtained with polydispersities (PDI's) between 1.1 and 1.8.

Polymerization of **4** with Grubbs Catalysts

Catalyst	[M]/[Ru]	Conversion (%)	Yield (%)	M_n	M_w	PDI
I	101	94.7	89.4	31200	34970	1.12
I	53	88.2	85.9	19200	21080	1.10
II	111	94.0	86.6	31950	52050	1.63
II	58	89.2	89.7	23660	33150	1.40

Studies of the ceramic conversion reaction of the ROMP-synthesized polymer **6** indicated that weight loss begins near 100°C and is essentially complete by 500°C to give a final char yield of 72%. Elemental analysis of a 1650°C char (B, 67.9%; C, 32.2%) corresponded to a $(B_4C)_{1.0}(C)_{0.75}$ composition. XRD analyses indicated that chars up to 1200°C were amorphous, but, while still retaining a substantial amorphous component, those samples pyrolyzed at 1300°C and 1650°C showed the characteristic boron carbide peaks along with graphite peaks at 26° and 42° 2-theta. The excess carbon in these chars undoubtedly retards boron carbide crystallization. As discussed in the Proposed Research section, because of its higher molecular weight, polymer **6** has unique properties that enable for the first time the electrospinning of boron carbide nanofiber ceramics.



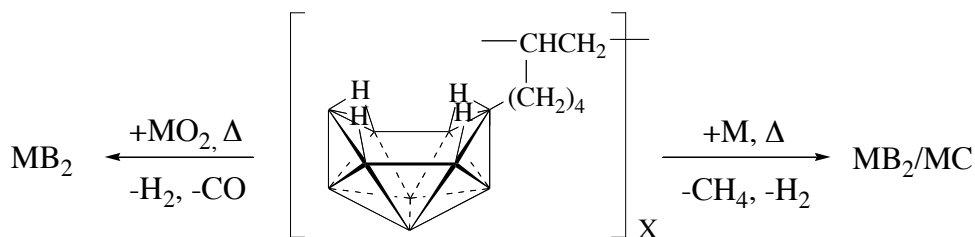
New Chemical Routes to Ultra High Temperature Ceramics

Hafnium and zirconium -borides, -carbides and -nitrides are high-melting, extremely hard solids with high thermal stabilities and chemical inertness.¹ As a result, they are important high heat- and wear-resistant materials for use in hostile environments, such as nose, leading-edge, and engine applications in hypersonic aerospace vehicles.^{2,3} Traditionally these materials have been prepared by high temperature powder techniques that are limited in their ability to generate processed materials with controlled compositions and properties. Our work during the last grant period has resulted in the development of new precursor systems for the efficient syntheses of hafnium and zirconium borides, as well as hafnium and zirconium -boride/carbide and -boride/nitride composites.⁴

Metal borides have classically been synthesized by a number of high temperature techniques, with one of the most common being the carbothermal reduction of metal oxides with boron carbide and carbon.¹



Although efficient, the carbothermal reduction can only be used to generate metal borides in powder form. Our work has now shown that polymer/metal dispersions employing the newly designed organoboron polymers, poly(hexenyldecaborane)⁵ and poly(norbornenyldecaborane)⁵, are useful precursor systems for the synthesis of both metal boride and metal-boride/carbide materials.



Metal-oxide/polymer dispersions were prepared by adding a metal oxide to a solution of the polymer, followed by solvent evaporation with ultrasonic agitation. Pyrolysis to 1450°C of hafnium-oxide and zirconium-oxide/poly(hexenyldecaborane) dispersions under argon produced hafnium and zirconium diborides in excellent chemical and ceramic yields. As illustrated in the Figure below for HfB₂, XRD analyses showed that HfB₂ and ZrB₂ were the only crystalline products.⁴

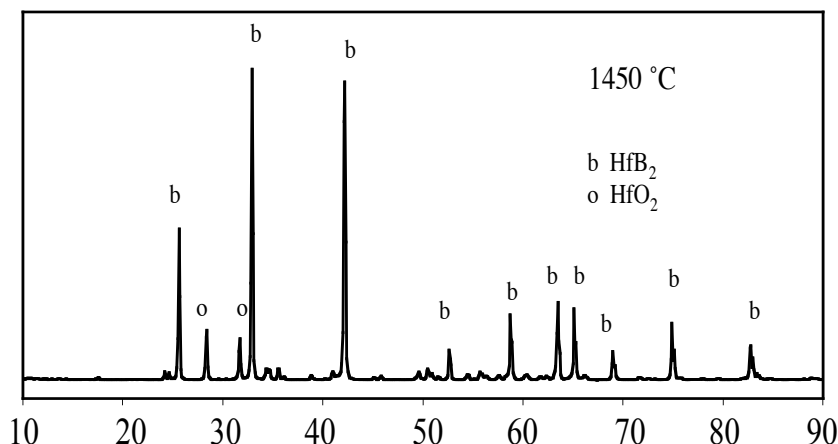
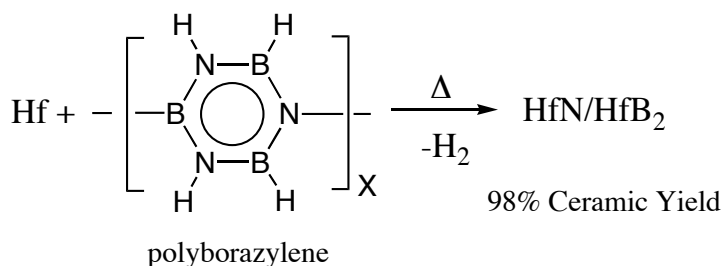


Figure 1. XRD analysis of a of HfO₂/poly(hexenyldecaborane) dispersion pyrolyzed at 1450 °C (2h)

Although much of the past work on ultra high temperature materials has focused on pure metal borides, the properties of composite metal-boride/carbide, as well as metal-boride/nitride systems, have been largely unexplored due to the inability to make such composites in a controlled and systematic fashion. However, we showed⁴ that pyrolyses of hafnium/poly(hexenyldecaborane) and zirconium/polyborazylene polymer dispersions provide

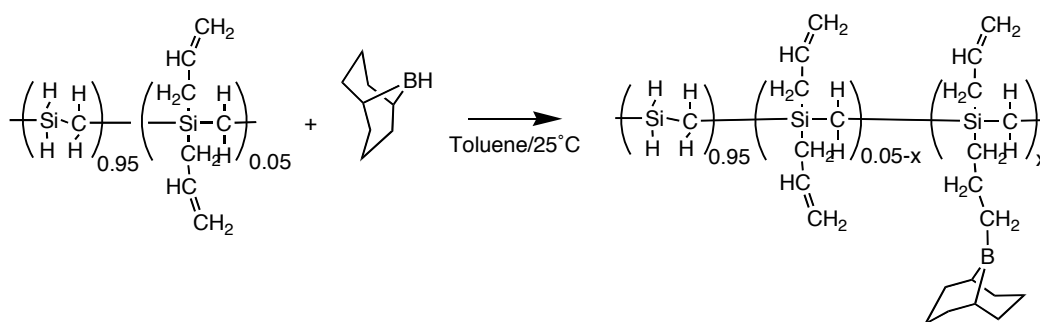
efficient synthetic routes to hafnium and zirconium-boride/carbide composites in high ceramic yields. Pyrolyses of hafnium/polyborazylene and zirconium /polyborazylene dispersions under argon likewise produce HfB_2/HfN and ZrB_2/ZrN ceramic composites in high ceramic yields.



While hafnium and zirconium boride/carbide and boride/nitride composite materials have previously been prepared by sintering powders at high temperatures, the polymer based routes discussed above are unique in their ability to produce composites composed of intimately mixed polycrystals, with grain sizes on the order of nanometers, in high ceramic and chemical yields. We are currently investigating the microstructure evolution and properties of these and related composite materials.

Synthesis and Ceramic Conversion Reactions of 9-BBN-Modified Allylhydridopolycarbosilane: A New Single-Source Precursor to Boron-Modified Silicon Carbide

Silicon carbide has many desirable properties, such as high strength and excellent corrosion and temperature stabilities that have enabled its use in many high-performance applications.^{16,17} The incorporation of <1 wt% boron into SiC ceramics has been shown to significantly improve sintering.¹⁸ We reported⁸ the design, synthesis, and properties of a new type of poly(borocarbosilane) polymer, 9-borabicyclo[3.3.1]nonane-modified allylhydridopolycarbosilane (AHPCS-9-BBN), that has proven to be an excellent processible single-source precursor to dense silicon carbide ceramics. As shown in the equation below, the polymers were synthesized in high yields by the reaction of allylhydridopolycarbosilane (AHPCS) with 9-borabicyclo[3.3.1]nonane (9-BBN).



The AHPCS-9-BBN polymers have thermal stabilities similar to that of the parent AHPCS polymer and thus maintain the processibility needed for their use as precursors to matrix materials. The ceramic yields of the AHPCS-9-BBN polymers were significantly higher than that of AHPCS due to an additional cross-linking reaction involving the 9-BBN substituent. Pyrolyses of the AHPCS-9-BBN polymers produced SiCB ceramics with boron contents ranging

from 0.1 to 0.8% depending upon the degree of polymer modification. In agreement with previous powder studies showing that small amounts of boron (<1%) can enhance SiC sintering, it was found that with increasing temperature, the AHPCS-9-BBN derived ceramics exhibited dramatic increases in their densities compared to those derived from the parent AHPCS. Thus, the AHPCS-9-BBN polymers are easily-synthesized, processible, single-source precursors to silicon carbide ceramics which have significantly higher densities than can be obtained from the parent AHPCS precursor.

Tough SiC-BN Composites Derived from AHPCS and Polyborazylene

In collaboration with Professor Len Interrante at RPI, we reported^{9,10} a new method that employs the immiscibility of polymer blends to prepare two-phase SiC-BN ceramic composites. Thus, co-pyrolysis to 1000°C of mixtures of the two polymeric precursors, allylhydridopolycarbosilane (AHPCS) (nominally, $[\text{Si}(\text{CH}_2\text{CH}=\text{CH}_2)_2\text{CH}_2]_{10.05}[\text{SiH}_2\text{CH}_2]_{0.95}$) and polyborazylene (PB) $[\text{B}_3\text{N}_3\text{H}_{4-x}]_n$, yielded amorphous SiC-BN ceramic composites whose microstructure resembles that of an immiscible polymer blend. A sample of a 50:50 mixture heated to 1600°C was shown to consist of a continuous SiC-rich phase with 20 atom % dissolved BN, and a dispersed BN-rich phase with 6 atom % SiC. In this sample, failure was found to occur at the interface and cracks are blunted at the weakly bonded second phase indicating unusual toughness for this precursor-derived SiC/BN composites. Such a system is of considerable interest as either an interphase or as the matrix phase in ceramic fiber-reinforced, ceramic matrix composites (such as $\text{SiC}_f/\text{SiC}_m$).

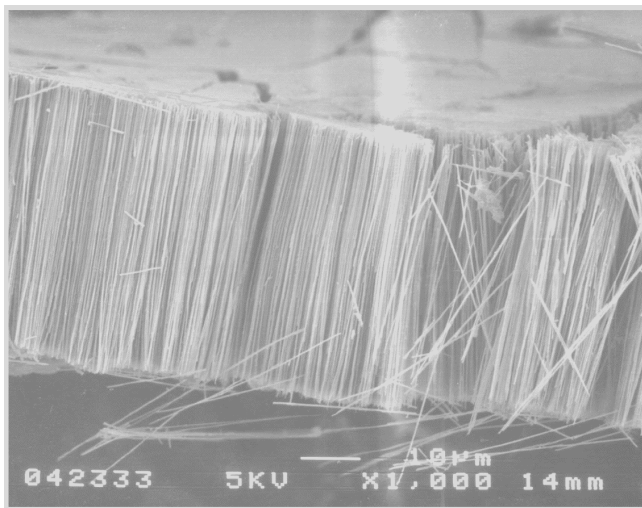
Organodecaborane Polymeric Precursors to Micro- and Nano-structured Ceramics

The polymer precursor route to ceramics has now been widely used to produce micron scale materials, but new technologies are demanding smaller sizes. Nanoscale ceramic materials are of particular interest due to their potential applications as electronic and optical devices, structural reinforcements, catalyst supports and membranes for gas separations.¹⁹ During the last grant period, we demonstrated that the new organodecaborane polymers described in the previous sections are high yield processable precursors to both micro- and nano-structured boron carbide ceramics.

Ceramic Micro- and Nano- Fibers and Cylinders

Owing to their small size, the traditional fiber spinning techniques that are used to produce micron scale fibers are inapplicable for the production of nanofibers. However, new porous alumina templating methods have recently been widely used to generate nanofibers from a variety of materials including polymers, carbon, metals, semiconductors and ceramics.²⁰ This template method involves the absorption of a precursor material into the channels of the nanoporous alumina using either gas-phase or solution methods, conversion of the precursors to the final solid state material by thermolytic or chemical reactions, and then dissolution of the alumina membrane to leave the free standing fibers. In our work, we used alumina membranes having a thickness of 60 μm and a nominal pore size of ~ 250 nm (± 50 nm). Boron carbide nanofibers were generated^{3,4,21} by initially filling the membranes with liquid 6,6'-(CH_2)₆-($\text{B}_{10}\text{H}_{13}$)₂ at 140°C, then pyrolyzing the filled templates at 1025°C to produce a boron carbide filled

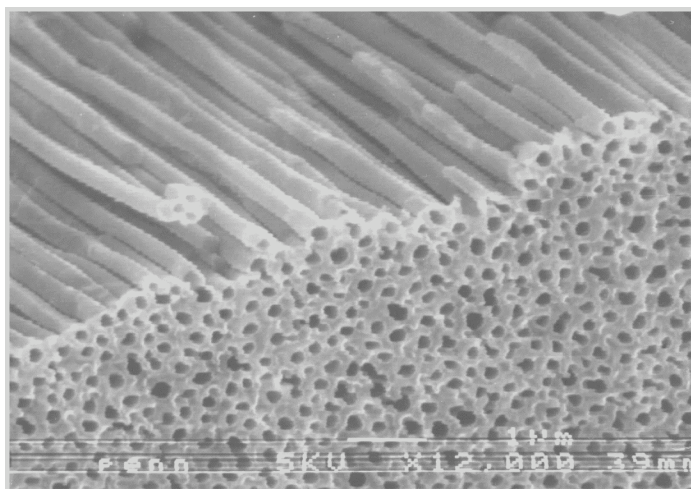
membrane. Immersing the sample in 48% hydrofluoric acid dissolved the alumina template. The scanning electron microscopy (SEM) image in the Figure to the right shows a sample of nanofibers prepared as described above. The fibers are uniform with an ~ 250 nm diameter and ~ 45 μ m length. X-ray diffraction studies of these fibers showed that while the 1000°C fibers are largely amorphous, the 1025°C fibers are composed of crystalline boron carbide. A thin layer of boron carbide was allowed to remain on one end of the fibers. This layer serves to hold the fibers in their parallel arrangement giving the highly aligned, brush-like configuration that is apparent in the Figure. As has been previously noted, one of the advantages of the templating technique over other methods for generating nanofibers is its natural ability to produce aligned, monodispersed ensembles of nanofibers.



Boron Carbide Nanofibers

We also showed that ceramic nanocylinders can be generated^{3,4} by a procedure similar to that reported by Martin²² for the production of polymer nanotubes. In order to avoid completely filling the channels of the porous alumina, the template is either only briefly dipped in the neat precursor or is treated with a precursor solution. Using the latter process, a toluene solution of the poly(hexenyldecaborane) precursor was vacuum filtered through the template. The solvent was then completely evaporated to leave a thin precursor layer on the surfaces of the membrane.

Pyrolysis of the coated membrane converted the precursor to a boron carbide coating. Dissolution of the coated alumina membranes with HF then yielded free-standing nanocylindrical boron carbide structures. The SEM image in the figure below shows a side view of an ensemble of boron carbide nanocylinders that are ~ 50 μ m long and ~ 250 nm in diameter and clearly shows the hollow cores of the cylindrical structures. The inside diameter and wall thickness of the nanocylinders can be controlled by the solution concentration and/or number of membrane treatments. Such hollow fiber structures are of great potential importance, since they could prove useful for the construction of multicomponent nanofibers.



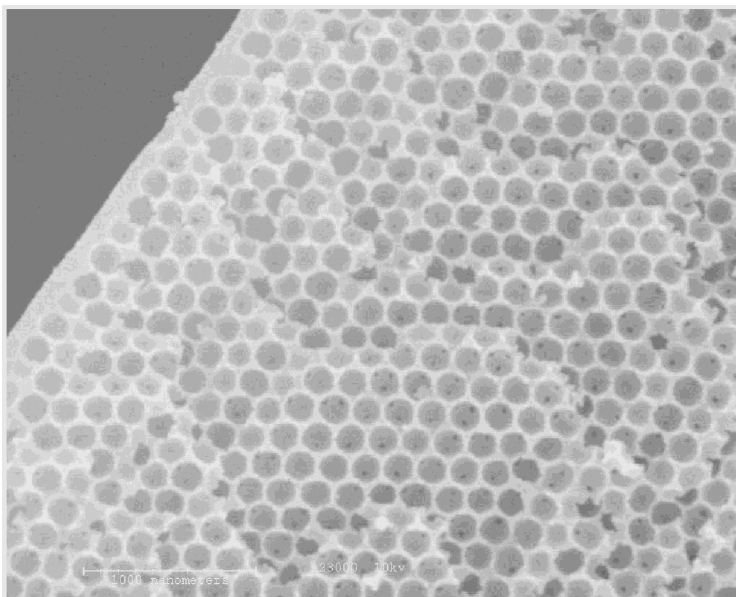
Boron Carbide Nanocylinders

We have similar used nanoporous alumina templating methods to generate nanofibers and nanocylinders of silicon carbide and boron nitride by employing the commercial-AHPCS and our polyborazylene²² precursor, respectively. However, it should be noted that alumina templating methods are limited to small-scales and larger scale methods are needed if such materials are to be used in real applications. In collaboration with Harry Allcock's group at Penn State University, we have been investigating the use of electrostatic spinning as a method of producing non-oxide ceramics nanofibers on much larger scales. Our initial work,^{11,12} which is described in more detail in the Proposed Research section, has shown that the use of such methods, in conjunction with a properly designed polymeric precursor, have great potential for the large scale production of these important materials.

Ordered Nanoporous Ceramics

The design of solids with ordered macroporosities has recently received great attention because of the possibility that such materials could serve as photonic bandgap and optical stop-gap materials, as well as catalyst supports and gas separation membranes.²³ Although methods for producing ordered porous materials with pore diameters less than 10 nm are well developed, only recently have techniques for producing uniform macroporous (>25 nm) materials been reported. These methods generally involve the controlled growth of a matrix around an ordered array of macroscale templates. Silica spheres, latex beads and triblock copolymers have each been employed as templates. Once the matrix structure is formed, the templates are then removed by either chemical etching or thermal decomposition to leave a macroporously ordered inorganic solid. For example, latex beads have been used as templates to construct, via sol-gel condensations, ordered macroporous arrays of titania, zirconia, and alumina. Other work employing the silica templates have yielded macroporous carbons.

We have now used this templating technique to make macroporous nonoxide ceramic structures.^{4,13} A macro-ordered silica array was first generated by employing the method recently reported by Colvin.²⁴ The open space in this framework was then filled with the boron-carbide precursor 6,6'-(CH₂)₆-(B₁₀H₁₃)₂ by immersion in a melt of the compound. Pyrolysis of the filled body to 1025°C, then yielded a boron carbide matrix surrounding the silica spheres. The silica spheres were then etched from the matrix by treatment with 48% HF to leave a “holey” boron-carbide framework.



Nanoporous Boron Carbide

The SEM image in the figure above shows a boron carbide framework with reasonably ordered ~50 nm pores. We are now optimizing our procedures to both increase the ordering of the framework and achieve control of the hole size (through the use of different size silica beads) of the boron carbide framework. As discussed in the Proposed Research Section, we have also successfully extended this method to the formation of both silicon carbide and boron nitride holey materials.

Recent AFOSR Sponsored Publications (2003-present)

1. M. J. Pender, K. M. Forsthoefel and L. G. Sneddon Molecular and polymeric precursors to boron carbide nanofibers, nanocylinders and nanoporous ceramics, *Pure and Applied Chemistry* 2003, 75: 1287-1294.
2. A. R. Puerta, E. E. Remsen, M. G. Bradley, W. Sherwood and L. G. Sneddon Synthesis and Ceramic Conversion Reactions of 9-BBN-Modified Allylhydridopolycarbosilane: A New Single-Source Precursor to Boron-Modified Silicon Carbide, *Chemistry of Materials*, 2003, 15: 478-485.
3. M. J. Pender, K. M. Forsthoefel and L. G. Sneddon, Molecular and polymeric precursors to boron carbide nanofibers, nanocylinders and nanoporous ceramics, in *Boron Chemistry at the Start of the 21st Century*, Y. Budnov, Ed., Royal Society: London, 2003.
4. K. Moraes, J. Vosburg, D. Wark, L. V. Interrante, A. R. Puerta, L. G. Sneddon and M. Narisawa, The Microstructure and Indentation Fracture of SiC-BN Composites Derived from Blended Precursors of AHPCS and Polyborazylene, *Chemistry of Materials*, 2004, 16: 125-132.
5. X. Wei, P. J. Carroll and L. G. Sneddon, A New route to Organodecaborane Polymers via Ruthenium-Catalyzed Ring Opening Metathesis Polymerization, *Organometallics*, 2004, 23: 163-165.
6. K. Forsthoefel and L. G. Sneddon, Precursor Routes to Group 4 Metal Borides, and Metal Boride/Carbide and Metal Boride/Nitride Composites, *Journal of Materials Research*, 2004, 19: 6043-6049.
7. Sneddon, M. Pender, K. Forsthoefel, U. Kusari. and X. Wei, Design, synthesis and applications of chemical precursors to advanced ceramic materials in nanostructured forms, *Journal of the European Ceramic Society*, 2005, 25: 91-97.
8. D. Welma, H. Allcock, X. Wei and L. G. Sneddon, Preparation of Boron Carbide Nanofibers from a Poly(norbornenyldecaborane) Single-Source Precursor via Electrostatic Spinning, *Advanced Materials*, 2005, 17: 859-862.
9. D. T. Welna, X. Wei, J. D. Bender, N. R. Krogman, L. G. Sneddon and H. R. Allcock, Electrostatic Spinning, Pyrolysis, Characterization of Boron Carbide Nanofibers Prepared from Poly(norbornenyldecaborane) – A Polymeric Ceramic Precursor, *Materials Research Society Proceedings*, accepted.
10. X. Wei, D. T. Welna, J. D. Bender, L. G. Sneddon and H. R. Allcock, Design and synthesis of boron carbide and boron-carbide/silicon-carbide ceramics from poly(norbornenyldecaborane), *Materials Research Society Proceedings*, accepted.
11. Wei, X.; Carroll, P. J.; Sneddon, L. G. "Ruthenium Catalyzed ROMP Syntheses of Alkenylpolyboranes: New Single-Source Precursors to Boron Carbide" in preparation.
12. Kusari, U.; Sneddon, L. G. "Generation of Nanoporous Nonoxide Ceramics via Silica Bead Templating" in preparation.

References

1. (a) Pender, M.; Wideman, T.; Carroll, P. J.; Sneddon, L. G. *J. Am. Chem. Soc.* **1998**, *120*, 9108-9109. (b) Pender, M.; Carroll, P. J.; Sneddon, L. G. *J. Am. Chem. Soc.* **2001**, *123*, 12222-12231.
2. Pender, M.; Sneddon, L. G. *ACS Polymer Preprints* **2000**, *41*, 551-552.
3. (a) Pender, M. J.; Forsthoefel, K.; Sneddon, L. G. in *Group 13 Chemistry: Fundamental Research, Materials Science and Catalysis* Shapiro, P. and Atwood, D. eds., American Chemical Society Symposium Series, ACS: Washington, D. C., 2002, 168-180 and (b) Pender, M. J.; Sneddon, L. G. in preparation.
4. Sneddon, L. G.; Pender, M.; Forsthoefel, K.; Kusari, U.; Wei, X. *J. Eur. Ceram. Soc.* **2004**, *25*, 91-97.
5. Wei, X.; Carroll, P. J.; Sneddon, L. G. *Organometallics* **2004**, *23*, 163-5.
6. Wei, X.; Welna, D. T.; Bender, J. D.; Sneddon, L. G.; Allcock, H. R. *Mater. Res. Soc. Proc.* **2005**, accepted.
7. Puerta, A. R.; Remsen, E. E.; Bradley, M. G.; Sherwood, W.; Sneddon, L. G. *Chem. Mater.* **2003**, *15*, 478-485.
8. Interrante, L. V.; Moraes, K.; Liu, Q.; Lu, N.; Puerta, A. R.; Sneddon, L. G. *Pure and Applied Chem.* **2002**, *74*, 2111-2117.
9. Moraes, K.; Vosburg, J.; Wark, D.; Interrante, L. V.; Puerta, A. R.; Sneddon, L. G.; Narisawa, M. *Chem. Mater.* **2004**, *16*, 125-132.
10. Welma, D.; Allcock, H.; Wei, X.; Sneddon, L. G. *Adv. Mater.* **2005**, *17*, 859-862.
11. Welna, D. T.; Wei, X.; Bender, J. D.; Krogman, N. R.; Sneddon, L. G.; Allcock, H. R. *Mater. Res. Soc. Proc.* **2005**, accepted.
12. Kusari, U.; Sneddon, L. G. in preparation
13. For some recent reviews on the synthesis and properties of boron carbide, see: (a) Thevenot, F. *Key Eng. Materials* **1991**, 56-57, 59-58 (b) *Boron Rich Solids*; Emin, D.; Aselage, T.; Beckel, C. L.; Howard, I. A.; Wood, C. eds.; AIP Conf. Proc 140, Am. Inst. Phys.: New York, 1986 (c) *Boron Rich Solids*; Emin, D.; Aselage, T.; Switendick, A. C.; Morosin, B.; Beckel, C. L. eds.; AIP Conf. Proc 231, Am. Inst. Phys.: New York, 1991.
14. See, for example, (a) Wood, C. In *Boron Rich Solids*; Emin, D.; Aselage, T.; Beckel, C. L.; Howard, I. A.; Wood, C. eds.; AIP Conf. Proc 140, Am. Inst. Phys.: New York, 1986, pp. 362-372 and references therein. (b) Aselage, T. L.; Tallant, D. R.; Gieske, J. H.; Van Deusen, S. B.; Tissot, R. G. *The Physics and Chemistry of Carbides; Nitrides and Borides*, **1990**, 97.
15. For some reviews on metal-catalyzed ROMP reactions, see: (a) Grubbs, R. H.; Tumas, W. *Science* **1989**, *243*, 907-915. (b) Schrock, R. R. *Acc. Chem. Res.* **1990**, *23*, 158-165. (c) Buchmeiser, M. R. *Chem. Rev.* **2000**, *100*, 1565-1604. (d) Grubbs, R. H.; Trnka, Tina M.: *Acc Chem. Res.* **2001**, *34*, 18-29.
16. (a) *Fine Ceramic Fibers*; Bunsell, A. R.; Berger, M.-H., Eds.; Marcel Dekker: New York, 1999. (b) Narula, C. K. *Ceramic Precursor Technology and its Applications*; Marcel Dekker: New York, 1995.

17. (a) Yajima, S.; Hayashi, J.; Omori, M. *Chem. Lett.* **1975**, 931. (b) Yajima, S.; Hasegawa, Y.; Hayashi, J.; Iimura, M. *J. Mater. Sci.* **1978**, *13*, 2569-2576. (c) Hasegawa, Y.; Iimura, M.; Yajima, S.; M. *J. Mater. Sci.* **1980**, *15*, 720.
18. (a) Prochazka, S.; Scanlan, R. M. *J. Am. Chem. Soc.* **1975**, *58*, 72. (b) Greskovich, C.; Rosolowski, J. H. *J. Am. Ceram. Soc.* **1976**, *59*, 336-343. (c) Suzuki, H.; Hase, T. *J. Am. Ceram. Soc.* **1980**, *63*, 349-350. (d) Stutz, D. H.; Prochazka, S.; Lorenz, J. *J. Am. Ceram. Soc.* **1985**, *68*, 479-482. (e) Negita, K. *J. Am. Ceram. Soc.* **1986**, *69*, C-308-C-310. (f) Passing, G.; Riedel, R.; Petzow, G. *J. Am. Ceram. Soc.* **1991**, *74*, 642-645. (g) Cao, J. J.; MoberlyChan, W. J.; De Jonghe, L. C.; Gilbert, C. J.; Ritchie, R. O. *J. Am. Ceram. Soc.* **1996**, *79*, 461-469. (h) Vaßen, R.; Kaiser, A.; Förster, J.; Buchkremer, H. P.; Stöver, D. *J. Mater. Sci.* **1996**, *31*, 3623-3637. (i) Tenailleau, H.; Bourrat, X.; Naslain, R.; Tressler, R. E.; Giannuzzi, L. A. *J. Am. Ceram. Soc.* **1998**, *81*, 2037-2044. (j) Gu, H.; Shinoda, Y.; Wakai, F. *J. Am. Ceram. Soc.* **1999**, *82*, 469-472.
19. Nanoscale Science, Engineering and Technology, Research Directions Report of the Basic Energy Sciences Nanoscience/Nanotechnology Group, US Department of Energy, and references therein (1999).
20. See, for example: (a) Martin, C. R. *Science* **1994**, *266*, 1961-1966. (b) Martin, C. R. *Acc. Chem. Res.* **1995**, *28*, 61-68. (c) Martin, C. R. *Chem. Mater.* **1996**, *8*, 1739-1746 and references therein. (d) Lakshmi, B. B.; Patrissi, C. J.; Martin, C. R. *Chem. Mater.* **1997**, *9*, 2544-2550. (e) Cepak, V. M.; Hulteen, J. C.; Che, G.; Jirage, K. B.; Lakshmi, B. B.; Fisher, E. R.; Martin, C. R. *Chem. Mater.* **1997**, *9*, 1065-1067. (f) Che, G.; Lakshmi, B. B.; Martin, C. R.; Fisher, E. R.; Ruoff, R. S. *Chem. Mater.* **1998**, *10*, 260-267. (g) Klein, J. D.; Herrick, II, Robert, D.; Palmer, D.; Sailor, M. J. *Chem. Mater.* **1993**, *5*, 902-904. (h) Zelenski, C. M.; Dorhout, P. K. *J. Am. Chem. Soc.* **1998**, *120*, 734-742. (i) Zhang, Z.; Gekhtman, D.; Dresselhaus, M. S.; Ying, J. *Chem. Mater.* **1999**, *11*, 1659-1665. (j) V. M. Cepak, V. M.; Martin, C. R. *Chem. Mater.* **1999**, *11*, 1363.
21. Pender, M. J.; Sneddon, L. G. *Chem. Mater.* **2000**, *12*, 280-283.
22. (a) Fazen, P. J.; Remsen, E. E.; Carroll, P. J.; Beck, J. S.; Sneddon, L. G. *Chem. Mater.* **1995**, *7*, 1942-1956. (b) Fazen, P. J.; Beck, J. S.; Lynch, A. T.; Remsen, E. E.; Sneddon, L. G. *Chem. Mater.* **1990**, *2*, 96-97.
23. Materials Research Society Bulletin, 26 (2001) 608.
24. (a) Turner, M. E.; Trentler, T. J.; Colvin, V. J. *Adv. Mater.* **2001**, *13*, 180. (b) Jiang, P.; Bertone, J. F.; Hwang, K. S.; Colvin, V. L. *Chem. Mater.* **1999**, *11*, 2132. (c) Jiang, P.; Hwang, K. S.; Mittleman, D. M.; Bertone, J. F.; Colvin, V. L. *J. Am. Chem. Soc.* **1999**, *121*, 11630. (d) Stoeber, W.; Fink, A.; Bohn, E. *J. Coll. Interface Sci.* **1968**, *26*, 62.